



(12) **United States Patent**  
**Purayath et al.**

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(54) **AIR GAPS BETWEEN COPPER LINES**

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CPC ..... **H01L 21/7682** (2013.01); **C23C 2/006** (2013.01); **H01J 37/32357** (2013.01); **H01L 21/30655** (2013.01); **H01L 21/31116** (2013.01); **H01L 21/76205** (2013.01); **H01L 27/1087** (2013.01); **H01L 2221/101** (2013.01)

(57)

**ABSTRACT**

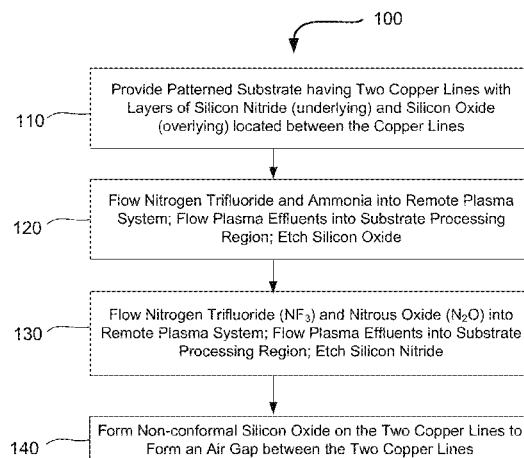
Methods are described for forming "air gaps" between adjacent copper lines on patterned substrates. The common name "air gap" will be used interchangeably the more technically accurate "gas pocket" and both reflect a variety of pressures and elemental ratios. The gas pockets may be one or more pores within dielectric material located between copper lines. Adjacent copper lines may be bordered by a lining layer and air gaps may extend from one lining layer on one copper line to the lining layer of an adjacent copper line. The gas pockets can have a dielectric constant approaching one, favorably reducing interconnect capacitance compared with typical low-K dielectric materials.

(58) **Field of Classification Search**

None

See application file for complete search history.

**15 Claims, 6 Drawing Sheets**



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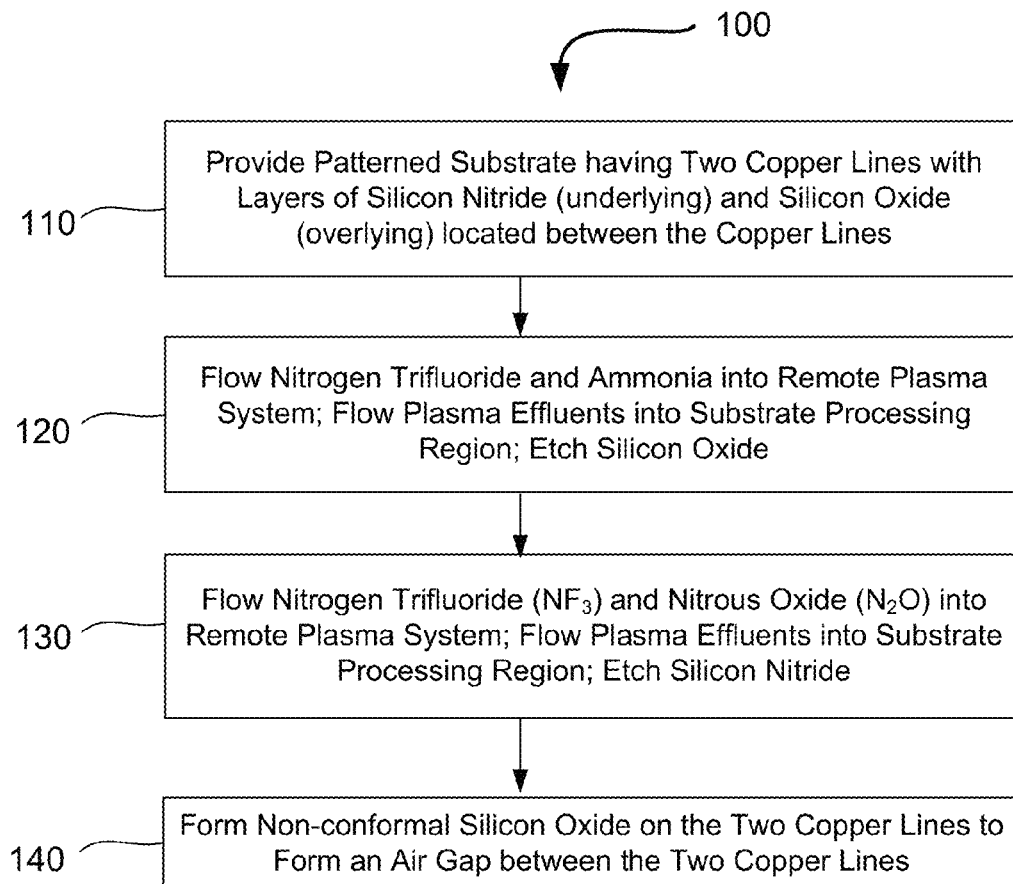
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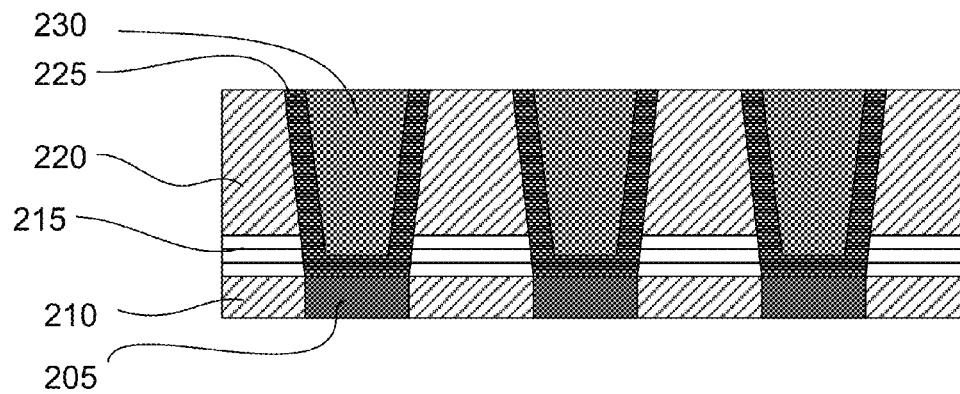
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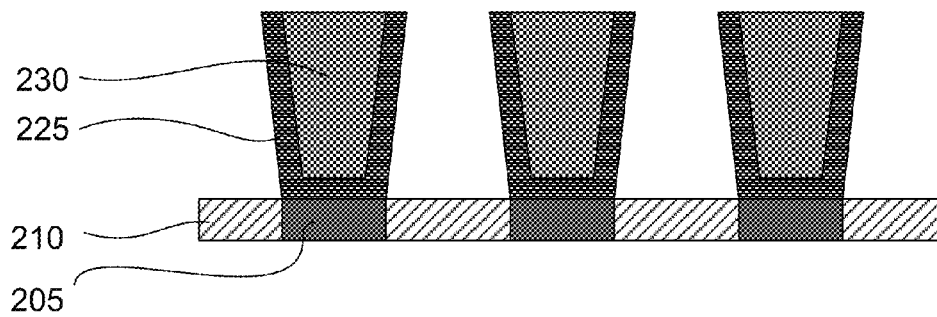
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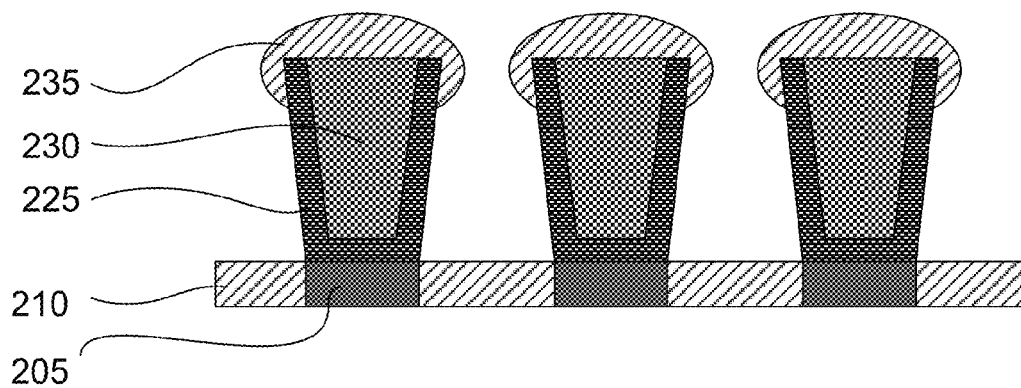
**FIG. 1**



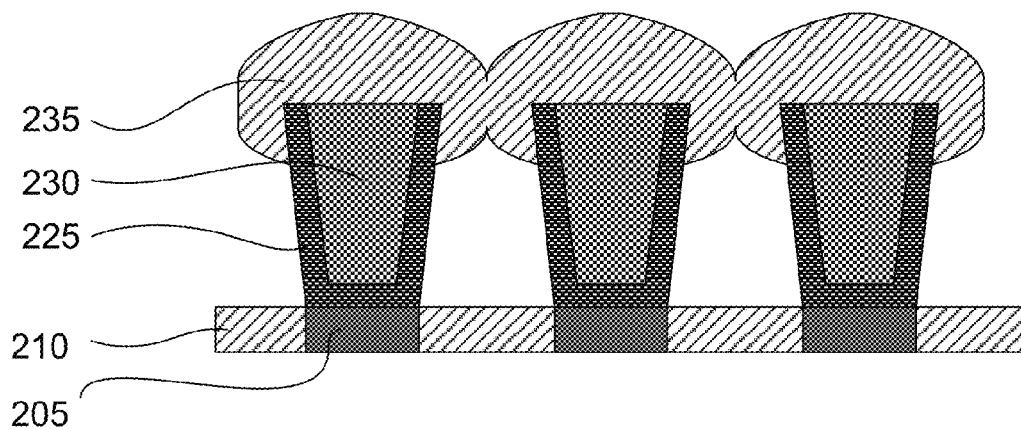
**FIG. 2A**



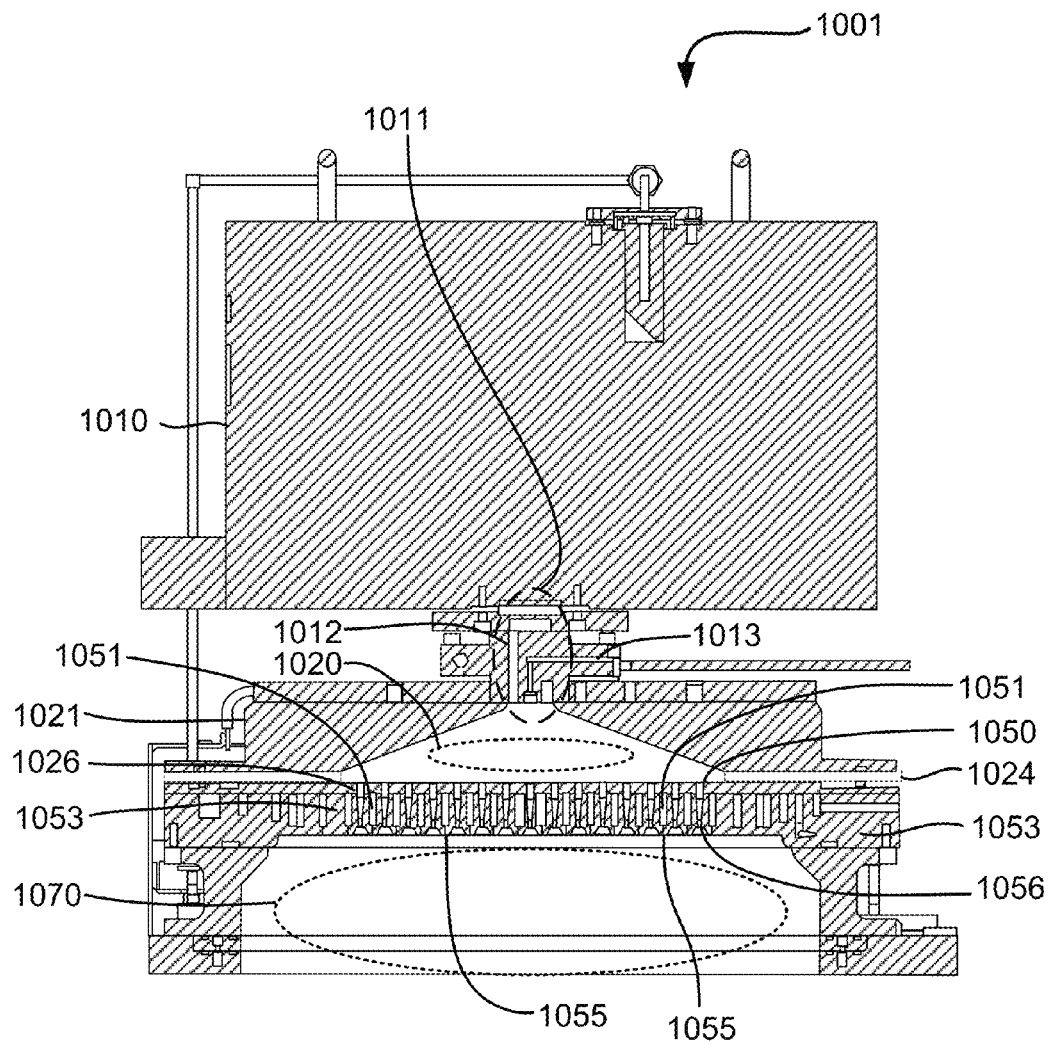
**FIG. 2B**



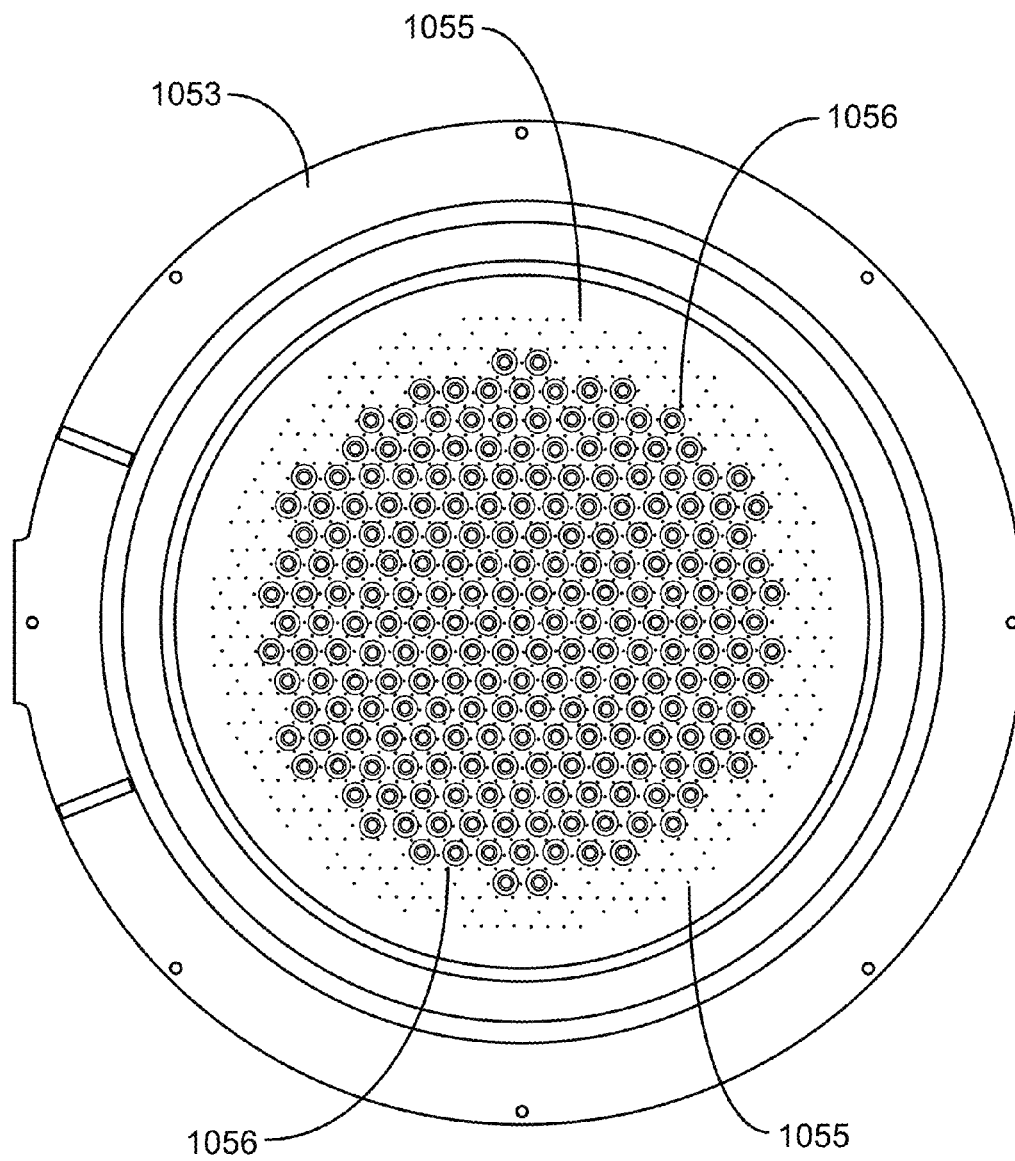
**FIG. 2C**



**FIG. 2D**

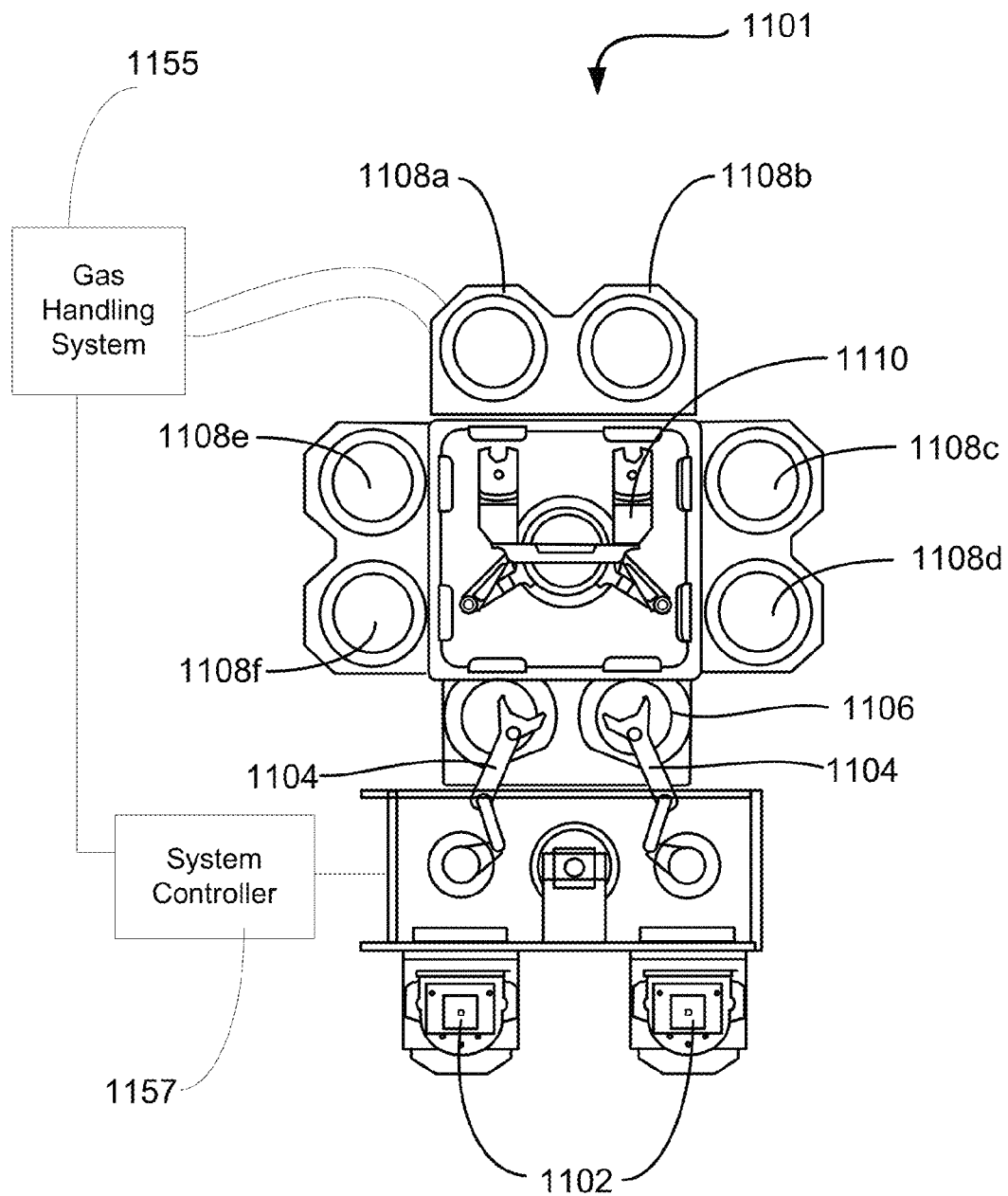


**FIG. 3A**



**FIG. 3B**





**FIG. 4**

## AIR GAPS BETWEEN COPPER LINES

## FIELD

Embodiments of the invention relate to formation of air gaps between copper lines.

## BACKGROUND

Semiconductor device geometries have dramatically decreased in size since their introduction several decades ago. Modern semiconductor fabrication equipment is routinely used to produce devices having geometries as small as 28 nm and less, and new equipment designs are continually being developed and implemented to produce devices with even smaller geometries. As device geometries decrease, the impact of interconnect capacitance on device performance increases. To reduce interconnect capacitance, inter-layer materials that have traditionally been formed of silicon oxide are being formed using lower dielectric constant materials (low k materials). Some low k materials that have been used include fluorinated silicon oxide, carbonated silicon oxide, and various polymers and aerogels. While these and other low k materials have been used successfully in the manufacture many different types of integrated circuits, new and improved processes that can create regions of low dielectric constant material between adjacent metal lines on substrates are desirable.

Copper lines are desirable because of their low resistivity. Using copper lines decreases signal loss but also raises the maximum frequency of operation for integrated circuits. The signal delay is proportional to the resistance of the copper lines times the capacitance between copper lines. However, it has been difficult to reduce the capacitance of the interlayer insulating layer used with copper interconnects due to process sequence integration issues.

Methods are needed to form gas pockets (generally referred to as air gaps) between copper lines in integrated circuits.

## SUMMARY

Methods are described for forming "air gaps" between adjacent copper lines on patterned substrates. The common name "air gap" will be used interchangeably the more technically accurate "gas pocket" and both reflect a variety of pressures and elemental ratios. The gas pockets may be one or more pores within dielectric material located between copper lines. Adjacent copper lines may be bordered by a lining layer and air gaps may extend from one lining layer on one copper line to the lining layer of an adjacent copper line. The gas pockets can have a dielectric constant approaching one, favorably reducing interconnect capacitance compared with typical low-K dielectric materials.

Embodiments of the invention include methods of forming air gaps between copper lines. The methods include transferring a patterned substrate into a substrate processing region. The patterned substrate includes two copper lines separated by a layer of silicon-containing dielectric. A portion of each of the two copper lines is exposed. The methods further include flowing a fluorine-containing precursor into a remote plasma region separated from the substrate processing region by a showerhead while forming a remote plasma in the remote plasma region to form plasma effluents. The methods further include flowing the plasma effluents into the substrate processing region to etch the silicon-containing dielectric from between the two copper lines. The methods further include forming a non-conformal layer of silicon oxide on the two

copper lines. Silicon oxide formed on each copper line grow and join together to trap an air gap between the two copper lines.

Embodiments of the invention include methods of forming air gaps between copper lines. The methods include transferring a patterned substrate into a first substrate processing system. The patterned substrate includes two copper lines separated by a layer of silicon nitride and an overlying layer of silicon oxide. A portion of each of the two copper lines is exposed. The methods further include flowing  $\text{NF}_3$  and  $\text{NH}_3$  into a first remote plasma region separated from the first substrate processing region by a showerhead while forming a first plasma in the first remote plasma region to form first plasma effluents. The methods further include flowing the first plasma effluents into the first substrate processing region to etch the overlying layer of silicon oxide from between the two copper lines. The methods further include flowing  $\text{NF}_3$  and  $\text{N}_2\text{O}$  into a second remote plasma disposed separated from a second substrate processing region by a showerhead while forming a second plasma in the second remote plasma region to produce second plasma effluents. The methods further include flowing the second plasma effluents into the second substrate processing region to etch the layer of silicon nitride from between the two copper lines. The methods further include forming a non-conformal layer of silicon oxide on the two copper lines. Silicon oxide formed on each copper line grow and join together to trap an air gap between the two copper lines.

Additional embodiments and features are set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the specification or may be learned by the practice of the embodiments. The features and advantages of the embodiments may be realized and attained by means of the instrumentalities, combinations, and methods described in the specification.

## DESCRIPTION OF THE DRAWINGS

A further understanding of the nature and advantages of the embodiments may be realized by reference to the remaining portions of the specification and the drawings.

FIG. 1 is a flow chart of an air gap process according to embodiments.

FIG. 2A is a cross-sectional view of a patterned substrate during an air gap process according to embodiments.

FIG. 2B is a cross-sectional view of a patterned substrate during an air gap process according to embodiments.

FIG. 2C is a cross-sectional view of a patterned substrate during an air gap process according to embodiments.

FIG. 2D is a cross-sectional view of a patterned substrate during an air gap process according to embodiments.

FIG. 3A shows a substrate processing chamber according to embodiments.

FIG. 3B shows a showerhead of a substrate processing chamber according to embodiments.

FIG. 4 shows a substrate processing system according to embodiments.

In the appended figures, similar components and/or features may have the same reference label. Further, various components of the same type may be distinguished by following the reference label by a dash and a second label that distinguishes among the similar components. If only the first reference label is used in the specification, the description is applicable to any one of the similar components having the same first reference label irrespective of the second reference label.

Methods are described for forming "air gaps" between adjacent copper lines on patterned substrates. The common name "air gap" will be used interchangeably the more technically accurate "gas pocket" and both reflect a variety of pressures and elemental ratios. The gas pockets may be one or more pores within dielectric material located between copper lines. Adjacent copper lines may be bordered by a lining layer and air gaps may extend from one lining layer on one copper line to the lining layer of an adjacent copper line. The gas pockets can have a dielectric constant approaching one, favorably reducing interconnect capacitance compared with typical low-K dielectric materials.

One way to form copper lines involves depositing copper into trenches and gaps in a patterned dielectric layer such as silicon oxide. This technique is referred to as copper damascene owing to its similarity to ancient decorative processes. Chemical mechanical polishing may be used to remove the copper located above the patterned dielectric layer. Air gaps may then be formed in between copper lines by etching away the patterned dielectric material. Until now, the copper had to be "capped" before etching away the patterned dielectric material, so the copper would not corrode.

The present invention involves etch processes which have been found to not corrode copper lines and therefore enable avoiding the capping process. The copper lines produced using the methods disclosed herein display less resistance, reduced RC delay, and enable faster switching speeds in completed devices. The methods of etching silicon oxide and/or silicon nitride from between the copper lines include remote plasmas and specific classes of precursors which have been found to be compatible with exposed copper. The plasmas effluents react with the patterned heterogeneous structures to selectively remove silicon oxide and/or silicon nitride. Therefore, exposed silicon may also be tolerated according to embodiments.

In order to better understand and appreciate the invention, reference is now made to FIG. 1 which is a flow chart of an air gap process 100 according to embodiments. Simultaneously, reference will be made to FIGS. 2A-2D which are cross-sectional views of a patterned substrate during the air gap process. Prior to the first operation, structures are formed in a patterned substrate. The structures include an underlying layer of patterned dielectric 210 and tungsten 205 (e.g. tungsten plugs). The structures further include an overlying patterned silicon nitride 215, patterned silicon oxide 220, a titanium liner 225 formed thereon and copper lines 230 formed on titanium liner 225. The structure is polished or otherwise processed to expose portions of patterned silicon oxide 220, titanium liner 225 and copper lines 230. The patterned substrate is then delivered into a substrate processing system in operation 110.

Nitrogen trifluoride and ammonia are flowed into a plasma region separate from a substrate processing region housing the patterned substrate (operation 120). The separate plasma region may be referred to as a remote plasma region herein and may be a distinct module from the processing chamber or a compartment within the substrate processing chamber separated from the substrate processing region by a showerhead. Remote plasma effluents (i.e. products from the remote plasma) are flowed through the showerhead into the substrate processing region and allowed to interact with the patterned substrate surface, also in operation 120, to remove patterned silicon oxide 220. Depending on the temperature of the patterned substrate, solid by-product may or may not be formed on any remaining patterned silicon oxide 220. If solid by-

products are formed, they are removed by heating the patterned substrate above the sublimation temperature (not shown in air gap process 100). The reaction-sublimation process may be repeated until patterned silicon oxide 220 is removed to expose patterned silicon nitride 215.

The estimated nature of the optional solid by-products is now described. Substrate temperatures which produce and do not produce solid residue will be described shortly. When produced the solid by-product may consume a top layer of the silicon oxide and the solid by-product possesses material from the plasma effluents and material from the silicon oxide. Plasma effluents produced from nitrogen trifluoride and ammonia include a variety of molecules, molecular fragments and ionized species. Currently entertained theoretical mechanisms of the formation of the solid by-product may or may not be entirely correct but plasma effluents are thought to include  $\text{NH}_4\text{F}$  and  $\text{NH}_4\text{F}\cdot\text{HF}$  which react readily with low temperature patterned silicon oxide 220. Plasma effluents may react with patterned silicon oxide 220, in embodiments, to form  $(\text{NH}_4)_2\text{SiF}_6$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  products. The  $\text{NH}_3$  and  $\text{H}_2\text{O}$  are vapors under the processing conditions described herein and may be removed from the substrate processing region by a vacuum pump. A layer of  $(\text{NH}_4)_2\text{SiF}_6$  solid by-product is left behind on the silicon oxide portion of the patterned substrate surface. The silicon (Si) originates from the exposed silicon oxide and the nitrogen, hydrogen and fluorine, which form the remainder of the  $(\text{NH}_4)_2\text{SiF}_6$ , originate from the plasma effluents. A variety of ratios of nitrogen trifluoride to ammonia into the remote plasma region may be used, however, between 1:1 and 4:1 or about a 2:1 ratio of ammonia to nitrogen trifluoride may be used according to embodiments.

Nitrogen trifluoride and ammonia are specific examples of a fluorine-containing precursor and a hydrogen-containing precursor. Generally speaking, a fluorine-containing precursor may be flowed into the remote plasma region and the fluorine-containing precursor may include one or more of atomic fluorine, diatomic fluorine, bromine trifluoride, chlorine trifluoride, nitrogen trifluoride, hydrogen fluoride, sulfur hexafluoride and xenon difluoride. Even carbon containing precursors, such as carbon tetrafluoride, trifluoromethane, difluoromethane, fluoromethane and other fluorocarbons, can be added to the group already listed. Similarly, a hydrogen-containing precursor flowed during operation 120 includes one or more of atomic hydrogen, molecular hydrogen, ammonia, a perhydrocarbon and an incompletely halogen-substituted hydrocarbon.

Between operation 120 and 130, the patterned substrate may be transferred between substrate processing chambers or may remain in the same substrate processing chamber according to embodiments. The removal of patterned silicon oxide 220 and patterned silicon nitride 215 may both occur in a Frontier™ processing chamber from Applied Materials, in which case no transfer is necessary. As described later, the concentration of ions is suppressed in the substrate processing region of a Frontier™ processing chamber by incorporating an ion suppression element. Operation 130 benefits from the use of the ion suppression element. However, patterned silicon oxide 220 may be removed using a Frontier™ or a Siconi™ processing chamber (also available from Applied Materials). The Siconi™ chamber which operates at much lower plasma frequencies, has no ion suppression element, and has integrated sublimation capabilities. The patterned substrate may also be transferred between separate substrate processing systems provided a continuous inert environment is provided for the substrate (i.e. no air-break is necessary).

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during transfer). The exposed copper would be corroded if exposed to an atmosphere containing oxygen.

Silicon nitride is removed in operation **130**. Flows of nitrogen trifluoride and dinitrogen oxide ( $N_2O$ ) are introduced into the remote plasma region. During this stage, little or no hydrogen is co-introduced into the remote plasma region according to embodiments. This second fluorine-containing precursor may not be mixed with a source of hydrogen, in embodiments, and the second plasma effluents may then be essentially devoid of hydrogen. A small amount of ammonia or hydrogen (e.g. less than 1:5 or 1:10 H:F atomic flow ratio) may be without corroding the exposed portion of copper lines **230**. Other sources of fluorine may be used to augment or replace the nitrogen trifluoride. In general, a second fluorine-containing precursor may be flowed into the plasma region and the second fluorine-containing precursor comprises at least one precursor selected from the group consisting of atomic fluorine, diatomic fluorine, bromine trifluoride, chlorine trifluoride, nitrogen trifluoride, hydrogen fluoride, sulfur hexafluoride, xenon difluoride, carbon tetrafluoride, trifluoromethane, difluoromethane, fluoromethane and fluorinated hydrocarbons. The plasma effluents formed in the remote plasma region are then flowed into the substrate processing region (also operation **130**) and patterned silicon nitride **215** is selectively etched from the patterned substrate.

A non-conformal silicon oxide layer **235** is then deposited on the two copper lines **230** using a process with a very high sticking coefficient and low mobility in operation **140**. An exemplary process is a typical plasma-enhanced chemical vapor deposition (PECVD) silicon oxide deposition process having high deposition rate. Depositing non-conformal silicon oxide **235** in this way grow and join together to trap an air gap (gas pocket) between the two copper lines.

The temperature of the patterned substrate during operation **120** may be below one of 60° C., 50° C., 40° C. or 35° C. in embodiments. The solid by-product formed during the first dry etch stage is removed prior to operation **130** by sublimation. The temperature of the solid by-product and the patterned substrate may be raised above one of 90° C., 100° C., 120° C. or 140° C. during the sublimation according to embodiments. The temperature during operation **120** may also be maintained at a higher level which promotes the simultaneous sublimation of solid residue by-product or does not form solid residue by-product in the first place. Therefore, the temperature of the patterned substrate during operation **120** may be less than above one of 160° C., less than 140° C., less than 120° C. or less than 100° C. during the sublimation according to embodiments. Additional patterned substrate temperatures will be provided in the course of describing exemplary equipment.

During operation **130**, a nitrogen-and-oxygen-containing precursor may be used in place of the exemplary nitrous oxide ( $N_2O$ ). More generally, a nitrogen-and-oxygen-containing precursor is flowed into the remote plasma system and the nitrogen-and-oxygen-containing precursor may comprise at least one precursor selected from  $N_2O$ , NO,  $N_2O_2$ ,  $NO_2$ . The nitrogen-and-oxygen-containing precursor may also be a combination of a source of nitrogen (e.g.  $N_2$ ) and a source of oxygen ( $O_2$ ) according to embodiments. The nitrogen-and-oxygen-containing precursor may consist of nitrogen and oxygen in embodiments. The nitrogen-and-oxygen-containing precursor may consist essentially of or consist of nitrogen and oxygen. Some nitrogen-and-oxygen-containing precursors may be very electronegative and benefit a high plasma power to form oxidizing plasma effluents. The nitrous oxide may be excited in a supplementary plasma before flowing the oxidizing plasma effluents so-generated into another remote

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plasma used to also excite the fluorine-containing precursor. The supplementary remote plasma is upstream from the remote plasma region in that effluents generally flow from the supplementary remote plasma into the remote plasma region, but not vice versa. The nitrogen-and-oxygen-containing precursor and the fluorine-containing precursor may be excited in separate remote plasmas and first combine in the substrate processing region according to embodiments.

During operation **120**, the fluorine-containing precursor and/or the hydrogen-containing precursor may further include one or more relatively inert gases such as He,  $N_2$ , Ar, or another inert gas. Argon may be added to the plasma to make a plasma easier to form. Helium may be added to improve uniformity of the plasma and the subsequent process. In an embodiment, the fluorine-containing gas includes  $NF_3$  at a flow rate of between about 5 sccm (standard cubic centimeters per minute) and 300 sccm, at a flow rate of between about 10 sccm and 600 sccm (standard liters per minute), He at a flow rate of between about 0 sccm and 5 slm, and Ar at a flow rate of between about 0 sccm and 5 slm. During operation **130**, the fluorine-containing precursor and/or the nitrogen-and-oxygen-containing precursor may further include one or more relatively inert gases such as He,  $N_2$ , Ar, or another inert gas. Argon may be added to the plasma to make a plasma easier to form. Helium may be added to improve uniformity of the plasma and the subsequent process. In an embodiment, the fluorine-containing gas includes  $NF_3$  at a flow rate of between about 5 sccm (standard cubic centimeters per minute) and 300 sccm,  $N_2O$  at a flow rate of between about 250 sccm and 5 slm (standard liters per minute), He at a flow rate of between about 0 sccm and 5 slm, and Ar at a flow rate of between about 0 sccm and 5 slm. Little or essentially no  $NH_3$  (or other hydrogen-containing precursor) is flowed during operation **130** according to embodiments. The second remote plasma region and the second substrate processing region may be devoid of hydrogen during operation **130** in embodiments. Additional flow rate embodiments are provided in the course of describing exemplary equipment. One of ordinary skill in the art would recognize that other gases and/or flows may be used depending on a number of factors including processing chamber configuration, substrate size, geometry and layout of features being etched.

The flow of  $N_2O$  (or another nitrogen-and-oxygen-containing precursor) into the remote plasma system and then into the remote plasma region results in a flow of oxidizing plasma effluents (which contain radical-nitrogen-oxygen) into the substrate processing region. Plasma effluents will be used herein to encompass the fluorine-containing plasma effluents and the oxidizing plasma effluents. The oxidizing plasma effluents include radical-nitrogen-oxygen. The radical-nitrogen-oxygen is thought to contain nitric oxide (NO), which is too reactive to directly deliver to the substrate processing region. The radical-nitrogen-oxygen contains radicals which comprise nitrogen and oxide and may consist of nitrogen and oxide in embodiments. The radical-nitrogen-oxygen is a component of the plasma effluents which flow into the substrate processing region in operation **130**. The plasma effluents also comprise radical-fluorine formed from the flow of the fluorine-containing precursor into the remote plasma region. The flow of radical-nitrogen-oxygen into the substrate processing region enables the radical-fluorine to remove the silicon nitride while limiting the reaction rate with exposed copper. The flow of radical-nitrogen-oxygen into the substrate processing region has little effect on the exposed regions of copper and the radical-fluorine is substantially unable to etch the copper.

During operation **120**, the method includes applying energy to the fluorine-containing precursor and the hydrogen-containing precursor in the remote plasma region to generate the plasma effluents. During operation **130**, the method includes applying energy to the fluorine-containing precursor and the nitrogen-and-oxygen-containing precursor in the remote plasma region to generate the plasma effluents. As would be appreciated by one of ordinary skill in the art, the plasmas during either stage may include a number of charged and neutral species including radicals and ions. Operation **120** and operation **130** may be performed in the same substrate processing chamber or separate processing chambers. As such, the remote plasma region in operation **120** may generally be referred to as the first remote plasma region and the remote plasma region in operation **130** may be referred to as the second remote plasma region. The plasma may be generated using known techniques (e.g., RF, capacitively coupled, inductively coupled). In an embodiment, the energy is applied to the first remote plasma region using a capacitively-coupled plasma unit at a source power of between about 5 watts and 300 watts and a pressure of between about 0.2 Torr and 30 Torr. The energy is applied to the second remote plasma region using a capacitively-coupled plasma unit at a source power of between about 50 W and 1500 W and a pressure of between about 0.1 Torr and 15 Torr. The capacitively-coupled plasma unit may be disposed remote from a gas reaction region of the processing chamber. For example, the capacitively-coupled plasma unit and the plasma generation region may be separated from the gas reaction region by a showerhead and/or an ion suppressor.

More generally, the pressure within the first remote plasma region and the first substrate processing region during operation **120** may be below or about 50 Torr, below or about 30 Torr, below or about 20 Torr, below or about 10 Torr or below or about 5 Torr according to embodiments. The pressure in the first plasma region and the first substrate processing region during operation **120** may be above or about 0.1 Torr, above or about 0.2 Torr, above or about 0.5 Torr or above or about 1 Torr in embodiments. Any of the upper limits on temperature or pressure may be combined with lower limits to form additional embodiments. The pressure during the operation **120** may be higher than during operation **130** because of the reliance on precursor combinations to form the precursors which create the solid by-product. The pressure within the second remote plasma region and the second substrate processing region during operation **130** may be below or about 20 Torr, below or about 15 Torr, below or about 10 Torr, below or about 6 Torr or below or about 3 Torr according to embodiments. The pressure in the second plasma region and the second substrate processing region during operation **130** may be above or about 0.05 Torr, above or about 0.1 Torr, above or about 0.2 Torr or above or about 0.5 Torr in embodiments.

In air gap process **100** silicon oxide is removed in operation **120** and silicon nitride is removed in operation **130**, both between adjacent copper lines **230**. In embodiments, only silicon oxide or silicon nitride is present between adjacent copper lines **230**. As a consequence, only operation **120** or operation **130** is necessary in some cases. The term "silicon-containing dielectric" will be used to encompass air gap processes which contain only operation **120**, only operation **130** or both operations **120** and **130**. The silicon-containing dielectric may be silicon oxynitride in embodiments.

The exemplary copper lines of FIGS. 2A-2D have a titanium lining layer included, in part, to discourage diffusion of copper into the sensitive underlying electronic components. In general, the lining layer may be a variety of materials including titanium, titanium nitride, tantalum and tantalum

nitride. The air gap formed in air gap processes described herein may extend all the way to the lining layer bordering each of two adjacent copper lines in embodiments.

In embodiments, an ion suppressor as described in the exemplary equipment section may be used to provide radical and/or neutral species for selectively etching silicon nitride. The ion suppressor may also be referred to as an ion suppression element. In embodiments, for example, the ion suppressor is used to filter etching plasma effluents (including radical-fluorine) to selectively etch silicon nitride. The ion suppressor may be included in each exemplary process described herein. Using the plasma effluents, an etch rate selectivity of silicon oxide relative to silicon and silicon oxide may be achieved.

The ion suppressor may be used to provide a reactive gas having a higher concentration of radicals than ions. The ion suppressor functions to dramatically reduce or substantially eliminate ionically charged species traveling from the plasma generation region to the substrate. The electron temperature may be measured using a Langmuir probe in the substrate processing region during excitation of a plasma in the remote plasma region on the other side of the ion suppressor. In embodiments, the electron temperature may be less than 0.5 eV, less than 0.45 eV, less than 0.4 eV, or less than 0.35 eV. These extremely low values for the electron temperature are enabled by the presence of the showerhead and/or the ion suppressor positioned between the substrate processing region and the remote plasma region. Uncharged neutral and radical species may pass through the openings in the ion suppressor to react at the substrate. Because most of the charged particles of a plasma are filtered or removed by the ion suppressor, the substrate is not necessarily biased during operation **130**. Such a process using radicals and other neutral species can reduce plasma damage compared to conventional plasma etch processes that include sputtering and bombardment. The ion suppressor helps control the concentration of ionic species in the reaction region at a level that assists the process. Embodiments of the present invention are also advantageous over conventional wet etch processes where surface tension of liquids can cause bending and peeling of small features.

Additional process parameters are disclosed in the course of describing an exemplar processing chamber and system. Exemplary Processing Equipment

FIG. 3A is a substrate processing chamber **1001** according to embodiments. A remote plasma system **1010** may process the fluorine-containing precursor which then travels through a gas inlet assembly **1011**. Two distinct gas supply channels are visible within the gas inlet assembly **1011**. A first channel **1012** conducts a precursor that has just passed through the remote plasma system **1010** (RPS), while a second channel **1013** conducts a precursor that has bypassed the remote plasma system **1010**. The first channel **1012** conducts the nitrogen-and-oxygen-containing precursor and the second channel **1013** conducts the fluorine-containing precursor.

The lid (or conductive top portion) **1021** and a perforated partition **1053** are shown with an insulating ring **1024** in between, which allows an AC potential to be applied to the lid **1021** relative to perforated partition **1053**. The AC potential strikes a plasma in chamber plasma region **1020**. The radical-nitrogen-oxygen (i.e. plasma-excited nitrogen-and-oxygen-containing precursor) may travel through first channel **1012** into chamber plasma region **1020** and may be further excited by a plasma in chamber plasma region **1020**. The fluorine-containing precursor flows through second channel **1013** and is only excited by chamber plasma region **1020** and not RPS **1010**. The perforated partition (also referred to as a shower-

head) **1053** separates chamber plasma region **1020** from a substrate processing region **1070** beneath showerhead **1053**. Showerhead **1053** allows a plasma present in chamber plasma region **1020** to avoid directly exciting gases in substrate processing region **1070**, while still allowing excited species to travel from chamber plasma region **1020** into substrate processing region **1070**.

Showerhead **1053** is positioned between chamber plasma region **1020** and substrate processing region **1070** and allows plasma effluents (excited derivatives of precursors or other gases) created within remote plasma system **1010** and/or chamber plasma region **1020** to pass through a plurality of through-holes **1056** that traverse the thickness of the plate. The showerhead **1053** also has one or more hollow volumes **1051** which can be filled, in embodiments, with a precursor in the form of a vapor or gas (such as an oxidizing plasma effluents excited in RPS **1010**) and pass through small holes **1055** into substrate processing region **1070** but not directly into chamber plasma region **1020**. Small holes **1055** may be described as blind holes to convey that they are not fluidly coupled directly to chamber plasma region **1020** like through-holes **1056**. Showerhead **1053** is thicker than the length of the smallest diameter **1050** of the through-holes **1056** in this disclosed embodiment. To maintain a significant concentration of excited species penetrating from chamber plasma region **1020** to substrate processing region **1070**, the length **1026** of the smallest diameter **1050** of the through-holes may be restricted by forming larger diameter portions of through-holes **1056** part way through the showerhead **1053**. The length of the smallest diameter **1050** of the through-holes **1056** may be the same order of magnitude as the smallest diameter of the through-holes **1056** or less in embodiments.

Showerhead **1053** may be configured to serve the purpose of an ion suppressor as shown in FIG. 3A. Alternatively, a separate processing chamber element may be included (not shown) which suppresses the ion concentration traveling into substrate processing region **1070**. Lid **1021** and showerhead **1053** may function as a first electrode and second electrode, respectively, so that lid **1021** and showerhead **1053** may receive different electric voltages. In these configurations, electrical power (e.g., RF power) may be applied to lid **1021**, showerhead **1053**, or both. For example, electrical power may be applied to lid **1021** while showerhead **1053** (serving as ion suppressor) is grounded. The substrate processing system may include a RF generator that provides electrical power to the lid and/or showerhead **1053**. The voltage applied, to lid **1021** may facilitate a uniform distribution of plasma (i.e., reduce localized plasma) within chamber plasma region **1020**. To enable the formation of a plasma in chamber plasma region **1020**, insulating ring **1024** may electrically insulate lid **1021** from showerhead **1053**. Insulating ring **1024** may be made from a ceramic and may have a high breakdown voltage to avoid sparking. Portions of substrate processing chamber **1001** near the capacitively-coupled plasma components just described may further include a cooling unit (not shown) that includes one or more cooling fluid channels to cool surfaces exposed to the plasma with a circulating coolant (e.g., water).

In the embodiment shown, showerhead **1053** may distribute (via through-holes **1056**) process gases which contain oxygen, fluorine and/or nitrogen and/or plasma effluents of such process gases upon excitation by a plasma in chamber plasma region **1020**. According to embodiments, the process gas introduced into the remote plasma system **1010** and/or chamber plasma region **1020** may contain fluorine (e.g.  $F_2$ ,  $NF_3$  or  $XeF_2$ ). The process gas may also include a carrier gas such as helium, argon, nitrogen ( $N_2$ ), etc. Plasma effluents may include ionized or neutral derivatives of the process gas

and may also be referred to herein as radical-fluorine referring to the atomic constituent of the process gas introduced.

Through-holes **1056** are configured to suppress the migration of ionically-charged species out of the chamber plasma region **1020** while allowing uncharged neutral or radical species to pass through showerhead **1053** into substrate processing region **1070**. These uncharged species may include highly reactive species that are transported with less-reactive carrier gas by through-holes **1056**. As noted above, the migration of ionic species by through-holes **1056** may be reduced, and in some instances completely suppressed or essentially eliminated. Controlling the amount of ionic species passing through showerhead **1053** provides increased control over the gas mixture brought into contact with the underlying wafer substrate, which in turn increases control of the deposition and/or etch characteristics of the gas mixture. For example, adjustments in the ion concentration of the gas mixture can significantly alter its etch selectivity (e.g., silicon nitride: silicon etch ratios).

According to embodiments, the number of through-holes **1056** may be between about 60 and about 2000. Through-holes **1056** may have a variety of shapes but are most easily made round. The smallest diameter **1050** of through-holes **1056** may be between about 0.5 mm and about 20 mm or between about 1 mm and about 6 mm in embodiments. There is also flexibility in choosing the cross-sectional shape of through-holes, which may be made conical, cylindrical or combinations of the two shapes. The number of small holes **1055** used to introduce unexcited precursors into substrate processing region **1070** may be between about 100 and about 5000 or between about 500 and about 2000 in embodiments. The diameter of the small holes **1055** may be between about 0.1 mm and about 2 mm.

Through-holes **1056** may be configured to control the passage of the plasma-activated gas (i.e., the ionic, radical, and/or neutral species) through showerhead **1053**. For example, the aspect ratio of the holes (i.e., the hole diameter to length) and/or the geometry of the holes may be controlled so that the flow of ionically-charged species in the activated gas passing through showerhead **1053** is reduced. Through-holes **1056** in showerhead **1053** may include a tapered portion that faces chamber plasma region **1020**, and a cylindrical portion that faces substrate processing region **1070**. The cylindrical portion may be proportioned and dimensioned to control the flow of ionic species passing into substrate processing region **1070**. An adjustable electrical bias may also be applied to showerhead **1053** as an additional means to control the flow of ionic species through showerhead **1053**.

Alternatively, through-holes **1056** may have a smaller inner diameter (ID) toward the top surface of showerhead **1053** and a larger ID toward the bottom surface. Through holes **1056** may have a larger inner diameter toward the top surface of showerhead **1053** and a smaller inner diameter toward the bottom surface of the showerhead. In addition, the bottom edge of through-holes **1056** may be chamfered to help evenly distribute the plasma effluents in substrate processing region **1070** as the plasma effluents exit the showerhead and promotes even distribution of the plasma effluents and precursor gases. The smaller ID may be placed at a variety of locations along through-holes **1056** and still allow showerhead **1053** to reduce the ion density within substrate processing region **1070**. The reduction in ion density results from an increase in the number of collisions with walls prior to entry into substrate processing region **1070**. Each collision increases the probability that an ion is neutralized by the acquisition or loss of an electron from the wall. Generally speaking, the smaller ID of through-holes **1056** may be

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between about 0.2 mm and about 20 mm. According to embodiments, the smaller ID may be between about 1 mm and 6 mm or between about 0.2 mm and about 5 mm. Further, aspect ratios of the through-holes **1056** (i.e., the smaller ID to hole length) may be approximately 1 to 20. The smaller ID of the through-holes may be the minimum ID found along the length of the through-holes. The cross sectional shape of through-holes **1056** may be generally cylindrical, conical, or any combination thereof.

FIG. 3B is a bottom view of a showerhead **1053** for use with a processing chamber according to embodiments. Showerhead **1053** corresponds with the showerhead shown in FIG. 3A. Through-holes **1056** are depicted with a larger inner-diameter (ID) on the bottom of showerhead **1053** and a smaller ID at the top. Small holes **1055** are distributed substantially evenly over the surface of the showerhead, even amongst the through-holes **1056** which helps to provide more even mixing in embodiments.

An exemplary patterned substrate may be supported by a pedestal (not shown) within substrate processing region **1070** when fluorine-containing plasma effluents and oxygen-containing plasma effluents arrive through through-holes **1056** in showerhead **1053**. Though substrate processing region **1070** may be equipped to support a plasma for other processes such as curing, no plasma is present during the etching of patterned substrate, in embodiments.

A plasma may be ignited either in chamber plasma region **1020** above showerhead **1053** or substrate processing region **1070** below showerhead **1053**. A plasma is present in chamber plasma region **1020** to produce the radical-fluorine from an inflow of the fluorine-containing precursor. An AC voltage typically in the radio frequency (RF) range is applied between the conductive top portion (lid **1021**) of the processing chamber and showerhead **1053** to ignite a plasma in chamber plasma region **1020** during deposition. An RF power supply generates a high RF frequency of 13.56 MHz but may also generate other frequencies alone or in combination with the 13.56 MHz frequency.

The top plasma may be left at low or no power when the bottom plasma in the substrate processing region **1070** is turned on to either cure a film or clean the interior surfaces bordering substrate processing region **1070**. A plasma in substrate processing region **1070** is ignited by applying an AC voltage between showerhead **1053** and the pedestal or bottom of the chamber. A cleaning gas may be introduced into substrate processing region **1070** while the plasma is present.

The pedestal may have a heat exchange channel through which a heat exchange fluid flows to control the temperature of the substrate. This configuration allows the substrate temperature to be cooled or heated to maintain relatively low temperatures (from  $-20^{\circ}\text{C}$ . through about  $120^{\circ}\text{C}$ .). The heat exchange fluid may comprise ethylene glycol and water. The wafer support platter of the pedestal (preferably aluminum, ceramic, or a combination thereof) may also be resistively heated to achieve relatively high temperatures (from about  $120^{\circ}\text{C}$ . through about  $1100^{\circ}\text{C}$ .) using an embedded single-loop embedded heater element configured to make two full turns in the form of parallel concentric circles. An outer portion of the heater element may run adjacent to a perimeter of the support platter, while an inner portion runs on the path of a concentric circle having a smaller radius. The wiring to the heater element passes through the stem of the pedestal.

The chamber plasma region or a region in a remote plasma system may be referred to as a remote plasma region. In embodiments, the radical precursors (e.g. radical-fluorine and radical-nitrogen-oxygen) are formed in the remote plasma region and travel into the substrate processing region

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where the combination preferentially etches silicon nitride. Plasma power may essentially be applied only to the remote plasma region, in embodiments, to ensure that the radical-fluorine and the radical-nitrogen-oxygen (which together may be referred to as plasma effluents) are not further excited in the substrate processing region.

In embodiments employing a chamber plasma region, the excited plasma effluents are generated (or further excited in the case of the radical-nitrogen-oxygen) in a section of the substrate processing region partitioned from a deposition region. The deposition region, also known herein as the substrate processing region, is where the plasma effluents mix and react to etch the patterned substrate (e.g., a semiconductor wafer). The excited plasma effluents may also be accompanied by inert gases (in the exemplary case, helium). The substrate processing region may be described herein as "plasma-free" during the etch processes (operation **120** and **130**) of the patterned substrate. "Plasma-free" does not necessarily mean the region is devoid of plasma. A relatively low concentration of ionized species and free electrons created within the plasma region do travel through pores (apertures) in the partition (showerhead/ion suppressor) due to the shapes and sizes of through-holes **1056**. In some embodiments, there is essentially no concentration of ionized species and free electrons within the substrate processing region. The borders of the plasma in the chamber plasma region are hard to define and may encroach upon the substrate processing region through the apertures in the showerhead. In the case of an inductively-coupled plasma, a small amount of ionization may be effected within the substrate processing region directly. Furthermore, a low intensity plasma may be created in the substrate processing region without eliminating features of the forming film. All causes for a plasma having much lower intensity ion density than the chamber plasma region (or a remote plasma region, for that matter) during the creation of the excited plasma effluents do not deviate from the scope of "plasma-free" as used herein.

During either operation **120** or **130**, nitrogen trifluoride (or another fluorine-containing precursor) may be flowed into chamber plasma region **1020** at rates between about 5 sccm and about 500 sccm, between about 10 sccm and about 300 sccm, between about 25 sccm and about 200 sccm, between about 50 sccm and about 150 sccm or between about 75 sccm and about 125 sccm in embodiments. During operation **120**, ammonia (or another hydrogen-containing precursor) may be flowed into chamber plasma region **1020** at rates between about 10 sccm and about 1000 sccm, between about 20 sccm and about 600 sccm, between about 50 sccm and about 400 sccm, between about 100 sccm and about 300 sccm or between about 150 sccm and about 250 sccm in embodiments. During operation **130**, nitrous oxide (or another nitrogen-and-oxygen-containing precursor) may be flowed into remote plasma region **1010** and then chamber plasma region **1020** (in series) at rates greater than or about 250 sccm, greater than or about 500 sccm, greater than or about 1 slm greater than or about 2 slm or greater than or about 5 slm in embodiments.

Combined flow rates of fluorine-containing precursor and nitrogen-and-oxygen-containing precursor into the chamber may account for 0.05% to about 20% by volume of the overall gas mixture; the remainder being carrier gases. The fluorine-containing precursor and the nitrogen-and-oxygen-containing precursor are flowed into the remote plasma region but the plasma effluents have the same volumetric flow ratio, according to embodiments. In the case of the fluorine-containing precursor, a purge or carrier gas may be first initiated into the remote plasma region before those of the fluorine-containing gas to stabilize the pressure within the remote plasma region.

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Plasma power applied to the first remote plasma region and the second remote plasma region can be a variety of frequencies or a combination of multiple frequencies and may be different between the two remote plasmas. In the exemplary processing system the second remote plasma is provided by RF power delivered between lid **1021** and showerhead **1053**. The RF power applied to the first remote plasma region (RPS **1010** in the example) may be between about 250 watts and about 15000 watts, between about 500 watts and about 5000 watts, or between about 1000 watts and about 2000 watts in embodiments. The RF power applied to the second remote plasma region (chamber plasma region **1020** in the example) may be between about 10 watts and about 1500 watts, between about 20 watts and about 1000 watts, between about 50 watts and about 500 watts, or between about 100 watts and about 200 watts according to embodiments. The RF frequency applied in the exemplary processing system may be low RF frequencies less than about 200 kHz, high RF frequencies between about 10 MHz and about 15 MHz or microwave frequencies greater than or about 1 GHz according to embodiments. High frequencies may be used during operation **130** to remove silicon nitride and low frequencies may be used during operation **120** to remove silicon oxide.

The temperature of the substrate may be between about  $-30^{\circ}\text{C}$ . and about  $150^{\circ}\text{C}$ . during operations **120** and/or **130**. The etch rate has been found to be higher for the lower temperatures within this range. In embodiments, the temperature of the substrate during the etch processes described herein is about  $-20^{\circ}\text{C}$ . or more,  $0^{\circ}\text{C}$ . or more, about  $5^{\circ}\text{C}$ . or more or about  $10^{\circ}\text{C}$ . or more. The substrate temperatures may be less than or about  $150^{\circ}\text{C}$ ., less than or about  $100^{\circ}\text{C}$ ., less than or about  $50^{\circ}\text{C}$ ., less than or about  $30^{\circ}\text{C}$ ., less than or about  $20^{\circ}\text{C}$ ., less than or about  $15^{\circ}\text{C}$ . or less than or about  $10^{\circ}\text{C}$ . in embodiments. Any of the upper limits on temperature or pressure may be combined with lower limits to form additional embodiments.

Substrate processing region **1070**, remote plasma system **1010** or chamber plasma region **1020** can be maintained at a variety of pressures during the flow of carrier gases and plasma effluents into substrate processing region **1070**. The pressure within the substrate processing region is below or about 50 Torr, below or about 30 Torr, below or about 20 Torr, below or about 10 Torr or below or about 5 Torr. The pressure may be above or about 0.01 Torr, above or about 0.1 Torr, above or about 0.2 Torr, above or about 0.5 Torr or above or about 1 Torr in embodiments. Lower limits on the pressure may be combined with upper limits on the pressure to form additional embodiments. The data show an increase in etch rate as a function of process pressure and an associated increase in loading effect, which may or may not be desirable or tolerated for a given process flow.

In embodiments, the substrate processing chamber **1001** can be integrated into a variety of multi-processing platforms, including the Producer<sup>TM</sup> GT, Centura<sup>TM</sup> AP and Endura<sup>TM</sup> platforms available from Applied Materials, Inc. located in Santa Clara, Calif. Such a processing platform is capable of performing several processing operations without breaking vacuum. Processing chambers that may implement methods disclosed herein may include dielectric etch chambers or a variety of chemical vapor deposition chambers, among other types of chambers.

Processing chambers may be incorporated into larger fabrication systems for producing integrated circuit chips. FIG. 4 shows one such system **1101** of deposition, baking and curing chambers according to embodiments. In the figure, a pair of FOUPs (front opening unified pods) **1102** supply substrate substrates (e.g., 300 mm diameter wafers) that are received by

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robotic arms **1104** and placed into a low pressure holding areas **1106** before being placed into one of the wafer processing chambers **1108a-f**. A second robotic arm **1110** may be used to transport the substrate wafers from the low pressure holding areas **1106** to the wafer processing chambers **1108a-f** and back. Each wafer processing chamber **1108a-f**, can be outfitted to perform a number of substrate processing operations including the dry etch processes described herein in addition to cyclical layer deposition (CLD), atomic layer deposition (ALD), chemical vapor deposition (CVD), physical vapor deposition (PVD), etch, pre-clean, degas, orientation and other substrate processes.

The wafer processing chambers **1108a-f** may include one or more system components for depositing, annealing, curing and/or etching a dielectric film on the substrate wafer. In one configuration, two pairs of the processing chamber (e.g., **1108c-d** and **1108e-f**) may be used to deposit dielectric material on the substrate, and the third pair of processing chambers (e.g., **1108a-b**) may be used to etch the deposited dielectric. In another configuration, all three pairs of chambers (e.g., **1108a-f**) may be configured to etch a dielectric film on the substrate. Any one or more of the processes described may be carried out on chamber(s) separated from the fabrication system shown in embodiments.

The substrate processing system is controlled by a system controller. In an exemplary embodiment, the system controller includes a hard disk drive, a floppy disk drive and a processor. The processor contains a single-board computer (SBC), analog and digital input/output boards, interface boards and stepper motor controller boards. Various parts of CVD system conform to the Versa Modular European (VME) standard which defines board, card cage, and connector dimensions and types. The VME standard also defines the bus structure as having a 16-bit data bus and a 24-bit address bus.

System controller **1157** is used to control motors, valves, flow controllers, power supplies and other functions required to carry out process recipes described herein. A gas handling system **1155** may also be controlled by system controller **1157** to introduce gases to one or all of the wafer processing chambers **1108a-f**. System controller **1157** may rely on feedback from optical sensors to determine and adjust the position of movable mechanical assemblies in gas handling system **1155** and/or in wafer processing chambers **1108a-f**. Mechanical assemblies may include the robot, throttle valves and susceptors which are moved by motors under the control of system controller **1157**.

In an exemplary embodiment, system controller **1157** includes a hard disk drive (memory), USB ports, a floppy disk drive and a processor. System controller **1157** includes analog and digital input/output boards, interface boards and stepper motor controller boards. Various parts of multi-chamber processing system **1101** which contains substrate processing chamber **1001** are controlled by system controller **1157**. The system controller executes system control software in the form of a computer program stored on computer-readable medium such as a hard disk, a floppy disk or a flash memory thumb drive. Other types of memory can also be used. The computer program includes sets of instructions that dictate the timing, mixture of gases, chamber pressure, chamber temperature, RF power levels, susceptor position, and other parameters of a particular process.

A process for etching, depositing or otherwise processing a film on a substrate or a process for cleaning chamber can be implemented using a computer program product that is executed by the controller. The computer program code can be written in any conventional computer readable programming language: for example, 68000 assembly language, C,



C++, Pascal, Fortran or others. Suitable program code is entered into a single file, or multiple files, using a conventional text editor, and stored or embodied in a computer usable medium, such as a memory system of the computer. If the entered code text is in a high level language, the code is compiled, and the resultant compiler code is then linked with an object code of precompiled Microsoft Windows® library routines. To execute the linked, compiled object code the system user invokes the object code, causing the computer system to load the code in memory. The CPU then reads and executes the code to perform the tasks identified in the program.

The interface between a user and the controller may be via a touch-sensitive monitor and may also include a mouse and keyboard. In one embodiment two monitors are used, one mounted in the clean room wall for the operators and the other behind the wall for the service technicians. The two monitors may simultaneously display the same information, in which case only one is configured to accept input at a time. To select a particular screen or function, the operator touches a designated area on the display screen with a finger or the mouse. The touched area changes its highlighted color, or a new menu or screen is displayed, confirming the operator's selection.

As used herein "substrate" may be a support substrate with or without layers formed thereon. The patterned substrate may be an insulator or a semiconductor of a variety of doping concentrations and profiles and may, for example, be a semiconductor substrate of the type used in the manufacture of integrated circuits. Exposed "silicon" of the patterned substrate is predominantly Si but may include minority concentrations of other elemental constituents such as nitrogen, oxygen, hydrogen and carbon. Exposed "silicon nitride" of the patterned substrate is predominantly  $\text{Si}_3\text{N}_4$  but may include minority concentrations of other elemental constituents such as oxygen, hydrogen and carbon. Exposed "silicon oxide" of the patterned substrate is predominantly  $\text{SiO}_2$  but may include minority concentrations of other elemental constituents such as nitrogen, hydrogen and carbon. In some embodiments, silicon oxide films discussed herein consist essentially of silicon and oxygen.

The term "precursor" is used to refer to any process gas which takes part in a reaction to either remove material from or deposit material onto a surface. "Plasma effluents" describe gas exiting from the chamber plasma region and entering the substrate processing region. Plasma effluents are in an "excited state" wherein at least some of the gas molecules are in vibrationally-excited, dissociated and/or ionized states. A "radical precursor" is used to describe plasma effluents (a gas in an excited state which is exiting a plasma) which participate in a reaction to either remove material from or deposit material on a surface. "Radical-fluorine" (or "radical-oxygen" or "radical-nitrogen-oxygen") are radical precursors which contain fluorine (or oxygen or nitrogen & oxygen) but may contain other elemental constituents. The phrase "inert gas" refers to any gas which does not form chemical bonds in the film during or after the etch process. Exemplary inert gases include noble gases but may include other gases so long as no chemical bonds are formed when (typically) trace amounts are trapped in a film.

The terms "gap" and "trench" are used throughout with no implication that the etched geometry has a large horizontal aspect ratio. Viewed from above the surface, trenches may appear circular, oval, polygonal, rectangular, or a variety of other shapes. A trench may be in the shape of a moat around an island of material. The term "via" is used to refer to a low aspect ratio trench (as viewed from above) which may or may

not be filled with metal to form a vertical electrical connection. As used herein, a conformal etch process refers to a generally uniform removal of material on a surface in the same shape as the surface, i.e., the surface of the etched layer and the pre-etch surface are generally parallel. A person having ordinary skill in the art will recognize that the etched interface likely cannot be 100% conformal and thus the term "generally" allows for acceptable tolerances.

Having disclosed several embodiments, it will be recognized by those of skill in the art that various modifications, alternative constructions, and equivalents may be used without departing from the spirit of the disclosed embodiments. Additionally, a number of well known processes and elements have not been described to avoid unnecessarily obscuring the present invention. Accordingly, the above description should not be taken as limiting the scope of the invention.

Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limits of that range is also specifically disclosed. Each smaller range between any stated value or intervening value in a stated range and any other stated or intervening value in that stated range is encompassed. The upper and lower limits of these smaller ranges may independently be included or excluded in the range, and each range where either, neither or both limits are included in the smaller ranges is also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included.

As used herein and in the appended claims, the singular forms "a", "an", and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a process" includes a plurality of such processes and reference to "the dielectric material" includes reference to one or more dielectric materials and equivalents thereof known to those skilled in the art, and so forth.

Also, the words "comprise," "comprising," "include," "including," and "includes" when used in this specification and in the following claims are intended to specify the presence of stated features, integers, components, or steps, but they do not preclude the presence or addition of one or more other features, integers, components, steps, acts, or groups.

The invention claimed is:

1. A method of forming air gaps between copper lines, the method comprising:

transferring a patterned substrate into a substrate processing region, wherein the patterned substrate comprises two copper lines separated by a layer of silicon-containing dielectric, wherein a portion of each of the two copper lines is exposed;

forming plasma effluents by flowing a fluorine-containing precursor into a remote plasma region separated from the substrate processing region by a showerhead while forming a remote plasma in the remote plasma region; etching the silicon-containing dielectric from between the two copper lines by flowing the plasma effluents into the substrate processing region, wherein an electron temperature in the substrate processing region is less than 0.5 eV during the operation of flowing the plasma effluents into the substrate processing region and wherein the portion of each of the two copper lines is exposed without an overlying liner layer during the etching of the silicon-containing dielectric; and

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forming a non-conformal layer of silicon oxide on the two copper lines, wherein silicon oxide formed on each copper line grow and join together to trap an air gap between the two copper lines.

2. The method of claim 1 wherein the fluorine-containing precursor comprises a precursor selected from the group consisting of nitrogen trifluoride, hydrogen fluoride, atomic fluorine, diatomic fluorine, carbon tetrafluoride and xenon difluoride.

3. The method of claim 1 wherein the operation of flowing the fluorine-containing precursor into the remote plasma region further comprises flowing a hydrogen-containing precursor into the remote plasma region.

4. The method of claim 3 wherein the hydrogen-containing precursor comprises one of atomic hydrogen, molecular hydrogen, ammonia, a perhydrocarbon and an incompletely halogen-substituted hydrocarbon.

5. The method of claim 1 wherein the silicon-containing dielectric is silicon oxide.

6. The method of claim 1 wherein the operation of flowing the fluorine-containing precursor into the remote plasma region further comprises flowing a nitrogen-and-oxygen-containing precursor into the remote plasma region.

7. The method of claim 6 wherein the nitrogen-and-oxygen-containing precursor comprises one of  $N_2O$ ,  $NO$ ,  $NO_2$  or  $N_2O_2$ .

8. The method of claim 6 wherein the nitrogen-and-oxygen-containing precursor consists of nitrogen and oxygen.

9. The method of claim 1 wherein the silicon-containing dielectric is silicon nitride.

10. The method of claim 1 wherein the remote plasma is a capacitively-coupled plasma.

11. The method of claim 1 wherein the two copper lines are bordered by a lining layer and the air gap extends to the lining layer bordering each of the two copper lines.

12. A method of forming air gaps between copper lines, the method comprising:

transferring a patterned substrate into a first substrate processing region, wherein the patterned substrate comprises two copper lines separated by a layer of silicon nitride and a layer of silicon oxide on top of the layer of silicon nitride, wherein a portion of each of the two copper lines is exposed prior to transferring the patterned substrate into the substrate processing region;

forming first plasma effluents by flowing  $NF_3$  and  $NH_3$  into a first remote plasma region separated from the first substrate processing region by a showerhead while forming a first plasma in the first remote plasma region;

etching the overlying layer of silicon oxide from between the two copper lines by flowing the first plasma effluents into the first substrate processing region, wherein the portion of each of the two copper lines is exposed without an overlying liner layer during the etching of the overlying layer of silicon oxide;

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producing second plasma effluents by flowing  $NF_3$  and  $N_2O$  into a second remote plasma disposed separated from a second substrate processing region by a showerhead while forming a second plasma in the second remote plasma region;

etching the layer of silicon nitride from between the two copper lines by flowing the second plasma effluents into the second substrate processing region, wherein the portion of each of the two copper lines is exposed without an overlying liner layer during the etching of the layer of silicon nitride; and

forming a non-conformal layer of silicon oxide on the two copper lines, wherein silicon oxide formed on each copper line grow and join together to trap an air gap between the two copper lines.

13. The method of claim 12 wherein the first remote plasma region is the second remote plasma region and the first substrate processing region is the second substrate processing region.

14. The method of claim 12 wherein the first and second substrate processing regions are located in different substrate processing chambers and the patterned substrate is transferred from the first substrate processing region to the second substrate processing region between the operations of flowing the first plasma effluents and flowing the second plasma effluents.

15. A method of forming air gaps between copper lines, the method comprising:

transferring a patterned substrate into a substrate processing region, wherein the patterned substrate comprises two copper lines separated by a layer of silicon-containing dielectric, wherein a portion of each of the two copper lines is exposed prior to transferring the patterned substrate into the substrate processing region;

forming plasma effluents by flowing a fluorine-containing precursor into a remote plasma region separated from the substrate processing region by a showerhead while forming a remote plasma in the remote plasma region;

etching the silicon-containing dielectric from between the two copper lines by flowing the plasma effluents into the substrate processing region, wherein the portion of each of the two copper lines is exposed without an overlying liner layer during the etching of the silicon-containing dielectric, wherein an electron temperature in the substrate processing region is less than 0.5 eV during the operation of flowing the plasma effluents into the substrate processing region; and

forming a non-conformal layer of silicon oxide on the two copper lines, wherein silicon oxide formed on each copper line grow and join together to trap an air gap between the two copper lines.

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